Surface waters quality diagnosis at Atlimeyaya, Puebla, México

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Abstract

Atlimeyaya, Puebla is located inside area 1 of the CENAPRED (Prevention Disasters National Center) risk map, which centers on the Popocatepetl volcano. The location of Atlimeyaya shows that it is subjected to significant amounts of ash fall, which strongly impacts all surface water bodies. In this study 9 sites were chosen, which were sampled 5 times during 2014. Collected water samples were analysed for 21 physicochemical parameters and results were compared with Mexican regulations for drinking water. Additionally, the CENAPRED database was searched for volcanic emissions taking place before each sampling event. Statistical analysis was done using Minitab 17, dot plots allowed us to see how chemical concentrations were modified at each sampling event, and how the data are dispersed over the whole concentration range. These results correlated with the number of emission events reported by CENAPRED. Even though most of the chemical parameters allowed us to classify the sampled waters as high quality ones, it is true that the results obtained allowed us to claim that volcanic emissions either as ash or water vapour strongly impact onto surface waters in the following chemical parameters: pH values are between 6.24 and 9.72 units, fluoride range corresponds to 0.1–0.97 ppm, nitrate 0.1–16.2 ppm, nitrite 0–23 ppm, chemical oxygen demand 0–91 ppm, lead 0–0.107 ppm, cadmium 0–0.031 ppm and manganese 0–0.06 ppm.

Keywords: volcanic ash, surface water, chemical quality, toxicity.

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1 Introduction

Concern about environmental risks due to volcano emissions either as gas, vapour or ash has been worked through the evaluation of samples collected in sites on and nearby active volcanoes. Research has included efforts to get an insight into gas and aeorosol emissions; as well as to the collection, classification and analysis of ash particles. In addition, there has been some research about the leachate properties of volcanic ash by mixing it with either deionized or marine water. Some of the findings are summarized in the following paragraphs.

Menard *et al.* [1] reported sampling events in the years 2009, 2011 and 2012 using filter packs for collecting gas and aerosol at the outlet of fumaroles from Lascar volcano (Chile). Elution of chemical species from filters allowed for the detection of major gaseous species and trace elements. They found that SO_2, HCl and HF exhibit a broad concentration range (112–3530 mg m^{-3}, 16–935 mg m^{-3} and 0–494 mg m^{-3} respectively). They also found the presence of main trace elements, such as, Ti and B. These elements were also found in a water sample from the Talabre River, which is near the Lascar volcano. Otherwise, an analysis of lava dome samples showed the presence of oxides being mainly SiO_2 (58%), followed by total alkali (Na_2O+K_2O 5%), as well as elevated concentrations of water soluble elements (Sr, Ba, Rb, B, Li).

Witham *et al.* [2] elaborated an analysis about how plumes of basaltic, intermediate and silica tephra can scavenge main gases (H_2O, CO_2, SO_2, H_2, H_2S, CO, and HCl) by either chemical reaction, dry and wet deposition or adsorption. Later on, by contact with water all scavenged compounds can be solubilized. They also pointed out that magma type and eruption style influences the composition of both particles and the volcanic gas phase; a fact that is reflected in the adsorption and deposition characteristics. The authors mentioned that at the vicinity of volcano coagulation, deposition and dispersion of ash are partially controlled by wind and humidity; they also provided a set of recommendations to analyse ash particles leaching solutions.

Under the hypothesis that gas/aerosol–ash interaction is an interfacial process, that should leave diagnostic chemical imprints on the ash surface, Delmelle *et al.* [3] used X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to measure the elemental composition and speciation of 9 pristine dry-sieved fine ash samples. They found that ash particles are mainly composed of Si, Al, Fe, Mg, Ca, Na, Cl, S, F and they also provided an approach to set up probable reaction paths based on the three temperature zones concept (salt formation, surface adsorption, condensation) proposed by Oskarsson [4]; each zone with a specific reaction type involving acidic magmatic gases (SO_2, HCl, HF). These reactions could take place within eruption plumes and so far will favour rapid acid dissolution of the ash surface. They mentioned that formation of thin sulphate and halide deposits can be attributed to an acid-mediated ash dissolution followed by precipitation at the ash-liquid interface.

Bagnato *et al.* [5] collected and analysed 20 ash samples determining water soluble components which are mainly composed of SO_4, Ca, Cl, F. Also, they found that fresh ash (from an eruptive period) exhibited the most acidic pH, while the ones collected from previous deposits have higher pH, which could be attributed to soluble deposit losses.

An approach to estimate how fast metals and nutrients are solubilized from volcanic ash into water is given by Jones and Gislason [6]. They used 8 ash samples from 7 volcanoes of different age and eruption type; and three types of water (distilled, North Atlantic sea, Southern Ocean). They found that an initial pH reduction took place only in distilled water, because seawater composition acts, buffering the input of acid precursors from ash. With solubilized components, they determined the presence of volatiles (F, Cl, Br, SO_4); alkalis (Li, Na, K), alkali earths (Mg, Ca, Sr, Ba); other major components were (B, NO_3, NO_2, NH_4, Al, Si, P) and traces of minor elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Pb). An important observation is that, in the first hour, major nutrients (NO_2, NO_3, NH_4, P, Al, Si, Mn and Fe) are released between 40 and 90%. Also they mention that there is a potential of poisoning due to leaching of F, Al, Mn, Co, Ni, Cu, Zn, Cd, Ba and Pb. These elements potentially cause biogeochemical changes in surface waters due to acidification and release of toxic elements.

Another contribution to estimate hazards from ash deposition and leaching is given by Cronin *et al.* [7]. They collected fresh ash at different locations, mixed with water in two extraction ratios 1:20, and 1:100, and analysed the leachate. They found that all samples produced an acid pH (4.3–5.8), and major water extractable species were F, SO4, Cl, Ca, Mg, K, Na, while the minor extractable species were Al, As, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni and Zn. The leaching efficiency trend for acidic anions was Cl>SO4>F; otherwise, for major cations Mg presence is the higher one; and in minor cations, the most leachable was Mn. The authors indicated that there is a health threat from leachable elements because soluble concentrations can reach values above the threshold safety for drinking water.

In respect of the Popocatépetl volcano and its influence zone, there are relevant two works from Armienta *et al.* [8, 9]. Their geochemical observations on ash leachates are presented in timely form providing information to assessing a potential hazard due to volcanic activity. During the 1994–1996 period, samples collected after ash emissions were analysed by mixing with distilled water in a 1:25 ratio. They found that major ion concentrations correspond to Cl, F, SO_4, Ca, Mg, Na, K and also mentioned that SO_4 concentrations were higher than values reported for other volcanoes. Concerning minor cation concentrations, their findings included Mn, Ti, Co, Sb, Zn, Tl, Pb and Cd. In the second report [9] they traced particles during the 1996 eruption (coarse to fine particles) and the 1997 eruption (mostly fine particles) they did a follow up of leachable ions based on the eruption time and distance from the volcano. The main determined anion concentrations in order of importance were SO_4>Cl>F. The major cation concentration corresponds to Mo, Ti, Zn and Mn; and minor abundance corresponds to Pb, Co, V, Cu. They found that there is an inverse relationship between the distance from the source, grain size and residence time in the plume. Also, fine grains have a larger area/volume ratio which enhances volatiles adsorption, plus a longer residence time which allows a condensation process to take place onto particles.

In 2012, a study of surface waters in the Atlixco municipality was realized for the communities of San Baltazar Atlimeyaya and San Pedro Atlixco. Sampling took place in a zone between 10 and 17 km from the Popocatepetl volcano crater [10]. Surface water samples were collected and analysed for anions and metal content. Results were compared with standards given by the Mexican Norm for drinking water (NOM 127 SSA1), relevant findings indicate that water overcomes threshold values for NO_3, Na, Fe, Pb, Cd. A later study [11] was based on collecting ash samples after volcanic emission events during 2012 and 2013. This collection took place at the San Baltazar Atlimeyaya community and physicochemical characterization indicated that Pb concentration range between 10 and 22 g Ton^{-1}, while Cd was between 1.2 and 3.4 g Ton^{-1}, and both have a solubility higher, to 70%.

Based on the last information which provides evidence that vapour and aerosols as well as volcanic ashes have acidity precursors like SO_4, Cl and F. Also, from ashes leachate tests the soluble metallic content have been estimated which is represented mainly by Ca, Mg, Na, K, and others in minor concentrations like Mn, Ti, Co, Sb, Zn, Tl, Pb and Cd; the last two representing a high toxicity risk. And even though it is considered that health threats could exist only temporarily after ash emissions; although this assumption does not apply for communities close to the Popocatepetl, because starting in December 1994, it happens that events of water vapour, aerosol and ash emissions have been taking place with high frequency. Therefore, there is a possibility that ionic inputs from either vapour condensation or ash deposition could affect surface water quality. A view of the Popocatepétl and the communities at major risk are shown in Figure 1.

In this paper, results from a 5 months follow up of surface water quality in a community close to the Popocatepétl volcano crater are presented. This study was done for a community of less than 2000 habitants named San Baltazar Atlimeyaya, which is located 2179 m above sea level and, according to the Mexican Disaster Prevention National Center (CENAPRED) risk map, this community is located inside the higher risk area (#1). Water samples were collected at 9 fixed points, all located along the path of a perennial water body. Sampling events were done in May, June, August, September and October in 2014 (the location of sampling points are shown in Figure 1). Collected samples were analysed for 21 physicochemical parameters. The main purpose of this study was to define a base line to estimate health risks due to surface water consumption.

2 Methodology

Water samples were collected in clean receptacles, ice cooled and transported to the laboratory for analysis of the following parameters: pH and Electrical Conductivity (EC, µS cm^{-1}) which were done with conductronic instruments. Gravimetric techniques were applied to determine phenolphthalein alkalinity

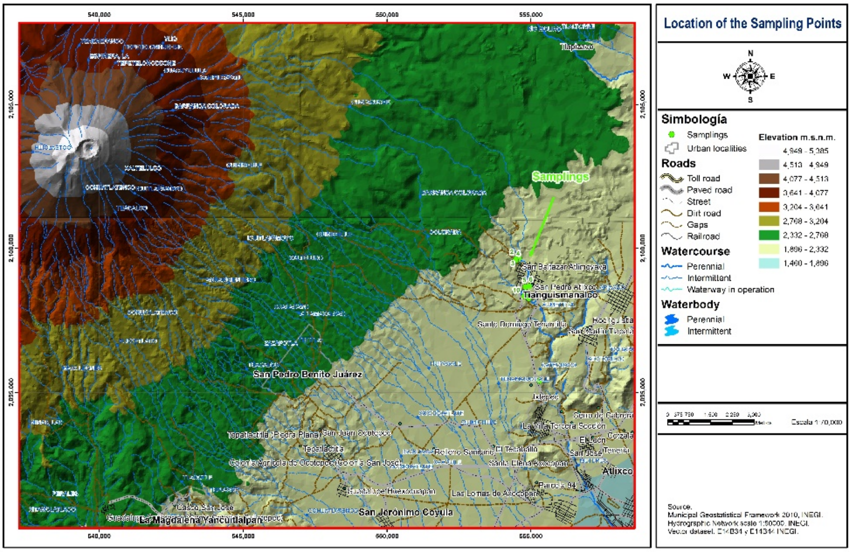

Figure 1: Aereal view of the Popocatépetl, and communities in risk zone 1.

(PhAlk, mg l^{-1}), Methyl Orange alkalinity (MOAlk, mg l^{-1}), total hardness (TH, mg l^{-1}), calcium hardness (CaH, mg l^{-1}), chloride (Cl, mg l^{-1}) and visible spectrophotometer HACH DR2500 was used to determine fluoride (F, mg l^{-1}), phosphate (PO_4, mg l^{-1}), nitrate (NO_3, mg l^{-1})), nitrite (NO_2, mg l^{-1}), sulphate (SO_4, mg l^{-1}) and chemical oxygen demand (COD, mg l^{-1}). Finally, an atomic absorption spectrophotometer GBC 232 was used to determine the main concern metal concentration of lead (Pb, mg l^{-1}), iron (Fe, mg l^{-1}), cadmium (Cd, mg l^{-1}), sodium (Na, mg l^{-1}), calcium (Ca, mg l^{-1}), potassium (K, mg l^{-1}), manganese (Mn, mg l^{-1}) and magnesium (Mg, mg l^{-1}).

In addition, the CENAPRED web page was consulted to download information of Popocatépetl activity during the week before each sampling event. The search was directed to look for gas, water vapour and ash emissions, as well as the intensity of the event (low, medium, high, explosive). Also searched for was the occurrence of tremor or volcano tectonic seismic activity.

A statistical analysis of the physicochemical parameters database was done with MINITAB 17 software.

3 Results and discussion

3.1 Volcanic emissions

The CENAPRED web page [12] provides information about emissions of gas and water vapour, ash emission, seismic activity and tremor occurrence. A search was undertaken, looking for data collected during the week before to the date in which the water collection was done (results are reported in Table 1). As can be observed, a lower number of events (less than 270) took place during May, June and September. In August, there were two peak emission days (199 and 407). Otherwise, in October there were no peak events, but there was ash emission, seismic activity, tremor and explosive events. In order of importance, the average events/day corresponds to August 112, October 70, May 31, September 25 and June 21.

Table 1: Volcanic events during the week previous to sampling.

Month	Gas and water vapor emission # events	Ash emission, # events	Seism, # events	Explosion, # events	Tremor, min
May	251	1	15	0	0
June	173	0	4	0	0
August	901	3	2	6	110
September	181	0	2	2	0
October	562	6	1	7	100

3.2 Water quality results

All water samples were tested for the 21 physicochemical parameters. Obtained results are compared in a dot plot graph because this kind of plot provides a better understanding of parameter response and its evolution through time. In the y axis legend sampling events are referred with the physicochemical parameter name and a number, being 1 for May, 2 for June, 3 for August, 4 for September, 5 for October.

pH results are presented in Figure 2, considering the normed values for drinking water are between 6.5 and 8.5, it can be observed that May and June have <30% values below the lower limit, dispersion between minimum and maximum values is <1 unit, also their average values (6.63, 6.72) are close to neutrality. For August, all data are close to neutrality, otherwise September and October have <35% values above the upper limit, and dispersion between minimum and maximum values is higher than 1.2 units. Their average values are near the upper limit of the allowed range (8.65, 8.37).

For Electrical Conductivity (EC), there are no reference values in the NOM 127, SSA1, but it can be observed that EC exhibit a decreasing trend from May to August, with a difference between minimum and maximum values <25 μS cm^{-1}. Otherwise, in September they increase, and values lie between 190 and 200 μS cm^{-1}, while in October all sites have a 200 μS cm^{-1} conductivity (results are shown in Figure 3).

Even though there is no reference in the NOM 127 for alkalinity, this was determined in both types: a) Phenolftalein Alkalinity (PhAlk) measured values were 0 from May to September, and only in October were values detected between 0 and 77.6 mg L^{1}, having 2 sites with 0 mg L^{1}. Also, the maximum value was registered in a site which corresponds to the union of an open canal effluent with the river; b) Methyl Orange Alkalinity (MOAlk) values exhibit an increasing trend from May to August; a unique value for September and the lower values with greater dispersion correspond to October; values lie between 15 and 110 mg L^{1}.

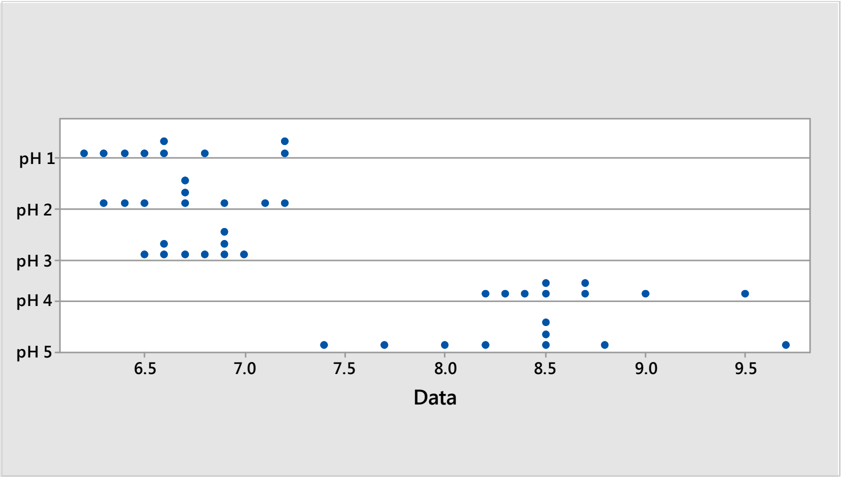

Figure 2: pH profiles being pH1 = May, pH2 = June, pH3 = August, pH4 = September, pH5 = October.

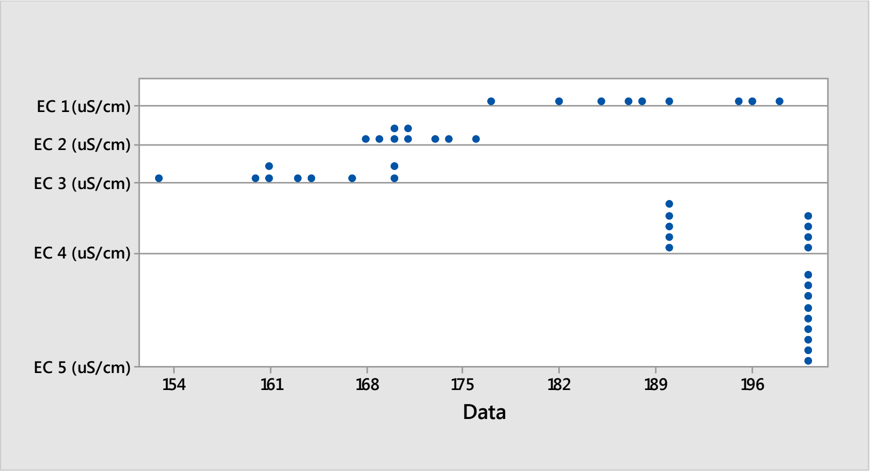

Figure 3: Electrical Conductivity (EC) profiles, being EC1 = May, EC2 = June, EC3 = August, EC4 = September and EC5 = October.

Total Hardness (TH) is a normed parameter with a maximum value of 500 mg L^1; none of the samples exceed this value. Although the higher values were detected during May in which TH ranges from 170 to 250 mg L^1, in later months TH tends to exhibit lower values; most of them between 20 and 140 mg L^{-1}. Although calcium hardness (CaH) is not regulated, higher values belong to August with 40–150 mg L^{-1}, followed by May between 60 and 100 mg L^{-1}. September and October values are between 20 and 50 mg L^{-1}, and June has no CaH.

Chloride (Cl) is a normed parameter with a maximum allowed concentration of 250 mg L^{-1}. This parameter exhibits a decreasing trend from May to August, and in October, maximum concentration is slightly higher than the one in May. In general, data does not overcome the threshold value, since data are spread between 0 and 37 mg L^{-1}.

Allowed fluoride (F) concentration in NOM 127 SSA1 is 1.5 mg L^{-1}. None of the measured concentrations is out of range; in general concentrations are between 0.1 and 0.48 mg L^{-1} from May to September, and it is in October when data exhibit greater dispersion (0.11-0.96 mg L^{-1}), and in this month only 1 point reaches the upper limit value.

In the NOM 127 SSA1 sulphate (SO_4) the maximum allowed concentration is 400 mg L^{-1}, determined values in all sampling are really low: 1–8 mg L^{-1}, and most of the data fall in the range of 6–8 mg L^{-1}. August is the sampling in which the lower value (1 mg L^{-1}) was found.

In phosphate (PO_4) there is no reference value in the NOM127 SSA1, although detected concentrations are really low (0.15–1.24 mg L^{-1}). The higher and more disperse ones are found in May, June and August; otherwise, September concentration ranges from 0.42–0.58 mg L^{-1}, while the lower values were found in October (0.15–0.47 mg L^{-1}).

Nitrate (NO_3) is a normed parameter, with a maximum allowed value of 10 mg L^{-1}. Most of the determined concentration values fall between 0 and 2.5 mg L^{-1}, and it happens that only in October that there were 2 critical sites; one with 10 mg L^{-1} and the other with 16.2 mg L^{-1}.

Nitrite (NO_2) maximum allowed concentration is 0.05 mg L^{-1}. For this parameter, all values are totally out of norm. The detected concentrations range was 0–23 mg L^{-1}. Months with lower concentration are May (0–2 mg L^{-1}) and October (0–3 mg L^{-1}). August and September exhibit similar concentrations (0–5 and 0–7 mg L^{-1}), and the higher ones took place in June (0–23 mg L^{-1}) with 5 of 9 data in the range of 10.5–23 mg L^{-1}.

Chemical Oxygen Demand (COD) is not a normed parameter. Minimum concentrations were found during June (0–4 mg L^{-1}) and August (0–10 mg L^{-1}). Similar ones are those of May (0–39 mg L^{-1}) and September (2–48 mg L^{-1}). The last exhibit showed more dispersion than May and the maximum values were found in October (47–91 mg L^{-1}).

The Iron (Fe) concentration normed value is 0.3 mg L^{-1}, detected concentrations are less than 20% of this reference value. Fe was mainly detected during May (0.009–0.045 mg L^{-1}), June (0–0.054 mg L^{-1}), and August

(0–0.033 mg L^{-1}), practically disappearing in September and October (0–0.006 mg L^{-1}).

For sodium (Na), the maximum allowed concentration is 200 mg L^{-1}, detected values are between 3 and 37 mg L^{-1}, and the maximum values were detected in the September samples; intermediate values in May and June and the lower ones correspond to August and October.

Calcium (Ca) is not a normed metal and detected concentrations are lower than those of sodium. For this metal concentration values range between 1.34 and 17.0 mg L^{-1}, minimal concentration during May and June, intermediate in August and September and higher ones in October.

Magnesium (Mg) also is a metal not normed, the determined concentration range for this metal is 4.09–9.09 mg L^{-1}, with the higher values in May and June, intermediate in September and October and the lower concentration was found in August.

Potassium (K) also is not normed metal, the detected concentrations range is 0.6–6.5 mg L^{-1}, although most of the data for all months can be found to be between 2 and 4.8 mg L^{-1}.

Manganese (Mn) was detected in very low concentrations 0.0–0.04 mg L^{-1}, which is less than 50% of de normed value of 0.15 mg L^{-1}, and again major concentrations were detected during October sampling. Intermediate values were registered in May, June and August, although 1 point in May registered 0.06 mg L^{-1}.

Lead (Pb) and cadmium (Cd) are the metals of higher concern. Pb maximum allowed concentration is 0.01 mg L^{-1}, and detected values are between 0.0 and 0.107 mg L^{-1}, although in May, June, August and September 30% of the sampled points have 0.0 mg L^{-1}, and the rest are mostly above the threshold value of 0.01 mg L^{-1}. Special attention is placed in October where the concentrations are higher than the normed value reaching up to 10 times the allowed concentration (results are shown in Figure 4).

Otherwise, cadmium (Cd) normed value is 0.005 mg L^{-1}, it happens that concentrations are between 0.0 and 0.031 mg L^{-1}, which is almost 6 times the maximum allowed concentration. Cd values below the maximum allowed occurs as follow: May has 8 sites, June only 1 site, August none, September 4, and October none. Maximum values of 0.031 mg L^{-1}, were recorded in May and June, while in October the maximum was 0.025 mg L^{-1}; in August 0.018 mg L^{-1}, also in September the maximum was 0.013 mg L^{-1} (results are shown in Figure 5).

4 Conclusions

From the above results it can be seen that main changes in water quality occur after August, which is the month with highest activity since it included two peak vapour emissions events and 1 day of tremor, although these events exerted minor affectation in pH, EC, and favour higher concentrations in CaH, PO_4, Fe, Cd and Ca. Otherwise, it is observed that in October there were less vapour emissions (60% in respect to August), but high volcanic activity combining

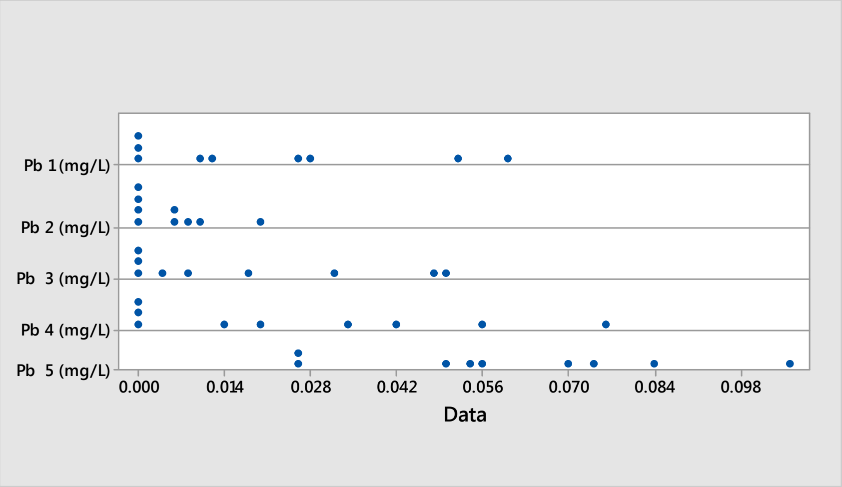

Figure 4: Lead concentration profiles, being Pb 1 = May, Pb 2 = June, Pb 3 = August, Pb 4 = September, Pb 5 = October.

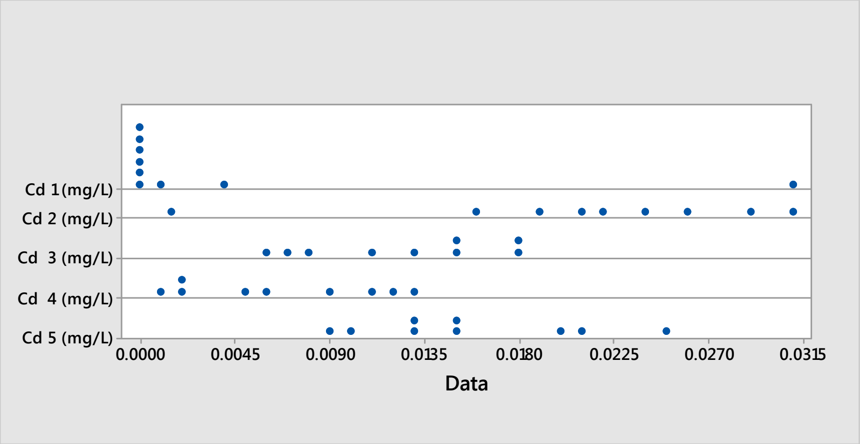

Figure 5: Cadmium (Cd) concentration profiles, being Cd 1 = May, Cd 2 = June, Cd 3 = August, Cd 4 = September, Cd 5 = October.

explosions, ash, seism and 4 days of tremor has favoured that pH, EC, PHAlk, Cl, F, SO_4, COD, Pb, Ca and K exhibited a displacement to higher values, while MOAlk, TH, CaH, PO_4, NO_2, Fe, Cd, Na, Ca and Mn, has been lowered in respect to September. It is important to notice that is necessary to increase the coverage of chemical parameters, as well as to make an effort to analyse chemical speciation to get a deep insight on interactions between parameters.

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